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Thermal Degradation of Poly(2,2-dialkyl-3-hydroxypropionic acid). 1. Living Depolymerization

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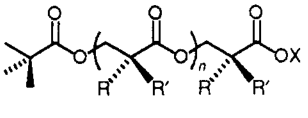
ABSTRACT: Poly(2,2-dialkyl-3-hydroxypropionic acid)s (usually prepared by living anionic polymerization of the corresponding 2,2-dialkyl-3-propiolactone) thermally degrade by two independent mechanisms depending on the state of the carboxylate group at the termination end of the polymer chain. When the carboxylate is deprotonated ($X = Li^+, Na^+, K^+, Cs^+, R_4N^+$, or R_4P^+) the polymer degrades predominantly by reverse polymerization. This paper concentrates on the reverse polymerization mechanism for polymer degradation. Reverse polymerization is dependent on the nucleophilicity of the terminal carboxylate group. This is demonstrated by the effect of the terminal counterion on the rate of degradation. Furthermore, reverse polymerization is shown to be a "living depolymerization". By living depolymerization we mean that all polymer chains degrade simultaneously from the living ends of the chains. Kinetics, change in MW distributions, and degradation of block copolymers are consistent with a living depolymerization.

Introduction

We have determined that poly(2,2-dialkyl-3-hydroxypropionic acid)s (I, often prepared by living anionic polymerization of the corresponding 2,2-dialkyl-3-propiolactone) thermally degrade by two independent mechanisms depending on the state of the carboxylate group at the termination end of the polymer chain. When the carboxylate is deprotonated ($X = Li^+, Na^+, K^+, Cs^+, R_4N^+$, or R_4P^+) the polymer degrades by attack of the nucleophilic carboxylate at the β-methylene position, forming volatile lactone. For polymer prepared by anionic ring-opening polymerization of the lactone, this degradation process is a reverse polymerization. We have demonstrated that this can be a "living depolymerization" under certain conditions. By living depolymerization we mean that all polymer chains degrade simultaneously from the living ends of the chains. In contrast, when the terminal carboxylate is protonated or esterified (X = H or R), polymer degradation is random-scission initiated.[1]



I

This paper demonstrates the reverse polymerization mechanism for degradation of poly(2,2-dialkyl-3-hydroxypropionic acid)s. A second paper will detail the random-scission-initiated degradation mechanism that occurs at higher temperatures (≳300 °C). A third paper supports the random scission mechanism by comparing results from computer models of the proposed mechanism with the observed results.[2]

Experimental Section

Polymer Synthesis. The 2,2-dialkyl-3-propiolactones were prepared by literature procedures.[14] Polymerizations were initiated by tetrabutylammonium pivalate (TBAP) in heptane or hexane at 70 °C. Initiator solutions were prepared by the addition of equimolar amounts of tetrabutylammonium hydroxide and pivalic acid to toluene followed by azeotropic removal of the methanol and water. The final volume was adjusted to give a 0.2 M solution of TBAP initiator in toluene. A typical polymerization was carried out as follows. To a 500-mL round-bottomed flask is added 200 mL of hexane, 38.4 g (0.3 mol) of 2-methyl-2-propyl-3-propiolactone, and 1.6 mL of 0.2 M TBAP initiator. The solution was heated at reflux (~2 h) until no lactone was detected by IR (1834 cm^{-1}). The solution was cooled and the polymer filtered from the hexane. The product had a M_n of 117 000 and M_w/M_n of 1.05. By adjusting the monomer/initiator ratio, polymers of varying MW were prepared, Table I.

Table I
Effect of Monomer/Initiator Ratio on Polymer MW

monomer/initiator	obsd DP	obsd M_n	M_w/M_n
50	51	6 560	1.07
100	102	13 100	1.07
200	206	26 400	1.07
500	610	78 100	1.09
2670	3170	405 800	1.09
5330	6140	786 000	1.13

Table II
Degradation of Poly-MPPL-COO$^-$ $^+$X (M_n = 117 000) Heated at 10 °C/min

X^+	(alkali ions)/(polymer chain)	peak deg temp, °C
H^+		390
Li^+	0.93 ± 0.2	369
Na^+	0.83 ± 0.05	365
K^+	1.03 ± 0.05	352
Cs^+	0.58 ± 0.05	341
PBu_4^+		268

Ion Exchange of the Terminal Carboxylate Group. The terminal carboxylate groups were protonated by adding 1 g of polymer and 1 g of acetic acid to 5 mL of THF. The polymer was precipitated by the addition of water and the precipitate was extensively washed with water. The polymer was dried in a drying pistol at 500 μmHg and 65 °C. Alkali ion exchange was achieved by adding 1 g of protonated polymer to 3 mL of THF along with a ~10-fold excess of base. The polymer was precipitated, washed, and dried as described above. Analysis indicated the polymer was more than 50% neutralized by this procedure in all cases, Table II.

Polymer Degradations. Isothermal polymer degradations were done in a Mettler TG 50 thermobalance purged with a steady flow of nitrogen or helium. Mass spectral analysis on the evolved gases was done with the TGA interfaced to a Hewlett-Packard 5970A mass-selective detector. A small portion of the gas evolved during degradation was drawn into the mass spec-

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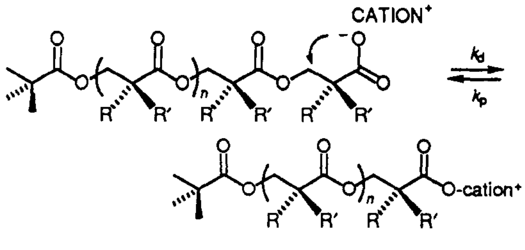
Scheme I

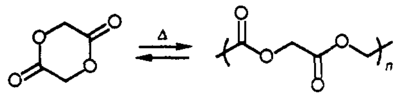


trometer inlet. A similar setup was used to obtian FTIR spectra of the evolved gases as a function of temperature.

Other Analyses. Molecular weights were determined by GPC using PMMA standards. NMR spectra were run in CDCl$_3$ with TMS as the internal standard on a GE QE-300 spectrometer. Alkali ion analysis on ion-exchanged polymers was done by Galbraith Laboratories Inc.

Results and Discussion

The thermal degradation of polylactones has interested polymer chemists almost as long as the lactone polymerization reaction. Bischoff and Walden in 1893 noted that poly(2,5-*p*-dioxanedione) (polyglycolide, III) reconverted to monomeric 2,5-*p*-dioxanedione (II) when heated in a vacuum.[3] After Drew and Haworth[4] reported the reversible polymerization of 2,3,4-trimethyl-*l*-arabonic acid, Carothers et al. published a systematic study of the reversible polymerization of six-membered cyclic esters.[5] Later studies showed that poly(ϵ-carpolactone)s also undergo thermal reverse polymerization to reform the seven-membered ring lactone.[6] However, poly(3-hydroxypropionic acid) does not reform the four-membered ring lactone but was found to undergo random-scission-initiated degradation above $\sim$150 °C, forming acrylic acid.[7,8] Apparently, abstraction of the acidic hydrogen α to the ester carbonyl occurs before the temperature is high enough to overcome the 25 kcal·mol^{-1} ring strain associated with reformation of 3-propiolactone.[9] Substitution of the acidic hydrogens in poly(3-hydroxypropionic acid) with methyl groups [poly(2,2-dimethyl-3-hydroxypropionic acid) or polypivalolactone] stabilizes the polymer[8] and apparently allows reformation of the lactone[10] and larger cyclic oligomers[11-13] under some conditions.



II III

A unique property of many polymers formed by ring-opening polymerization is the anisotropy along the polymer chain. For example, moving along an anionically polymerized poly(2,2-dialkyl-3-hydroxypropionic acid) chain (I) from the initiator end toward the termination end, we find that dialkyl carbon is encountered immediately prior to the carbonyl. This is in contrast to all vinyl polymers, and many condensation polymers, which are symmetrical (except for differences at the chain ends). One consequence of the chain anisotropy is that degradation by reverse polymerization should start at the termination end of the chain and proceed toward the initiator end, Scheme I. Our results demonstrate the effect chain anisotropy has on both reverse polymerization and random-scission-initiated thermal degradation.

We have taken advantage of the "living nature of anionic 2,2-dialkylpropiolactone polymerization to prepare polymer structures useful in elucidating the degradation mechanism.[15] For example, samples of poly(2-methyl-2-propyl-3-hydroxypropionic acid) (poly-MPPL) with various MWs and narrow MW distributions are easily prepared by adjusting the monomer/initiator ratio, Table I. The living nature of this polymerization makes the preparation of block copolymers very simple. We have used block copolymers to elucidate the direction of polymer degradation, i.e., whether degradation proceeds toward or away from the initiator end of the molecule.

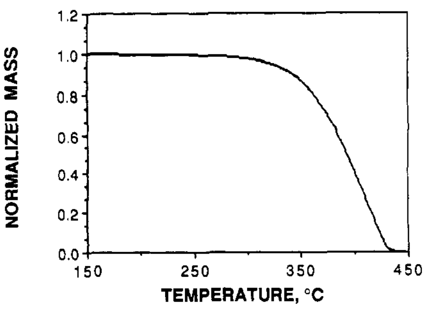
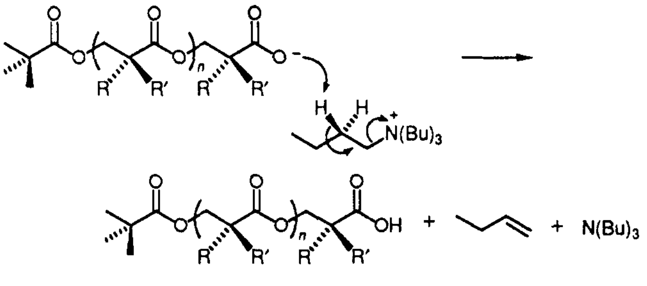


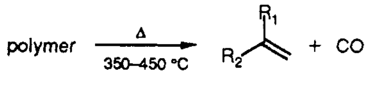
Figure 1. TGA of poly-MPPL-COO$^-$ $^+$NBu$_4$ heated at 10 °C/min.

Scheme II



Tetrabutylammonium pivalate initiated polymerization produces polymers with a pivalate unit at the initiation end and tetrabutylammonium carboxylate at the terminus (e.g., poly-MPPL-CO$^-$ $^+$NBu$_4$). For reasons that will be outlined later, the terminal carboxylate was ion exchanged (poly-MPPL-COOH, poly-MPPL-COO$^-$ Cs$^+$, etc.) or esterified (poly-MPPL-COOCH$_3$) for most of the degradation studies.

When poly-MPPL-COO$^-$ $^+$NBu$_4$ is heated at 10 °C/min, mass loss takes place between 300 and 440 °C, Figure 1. Degradation is very clean and mass loss is 100% within experimental error. The major products (>95%) are CO$_2$ and 2-methylpentene (2MP) as observed by mass spectrometry. We determined that polymer degradation is complicated by simultaneous degradation of the tetrabutylammonium carboxylate end group via Hofmann elimination, Scheme II. We observe the Hofmann elimination by ^{1}H NMR, Figure 2. Figure 2a–c is a series of NMR spectra taken of a tetramer sample before and after various degrees of heating. The initial spectrum (Figure 2a) shows peaks associated with Bu$_4$N$^+$ at $\sim$1.0, 1.45, 1.65, and 3.35 ppm of similar intensity to the oligomer protons. After heating to 150 °C for 30 min we observe a decrease in the Bu$_4$N$^+$ signal and a sample heated to 250 °C for 30 min shows no Bu$_4$N$^+$ signal. The results indicate that most of the COO$^-$ $^+$NBu$_4$ end groups are converted to COOH before polymer degradation ensues. However, at high heating rates some COO$^-$ $^+$NBu$_4$ end



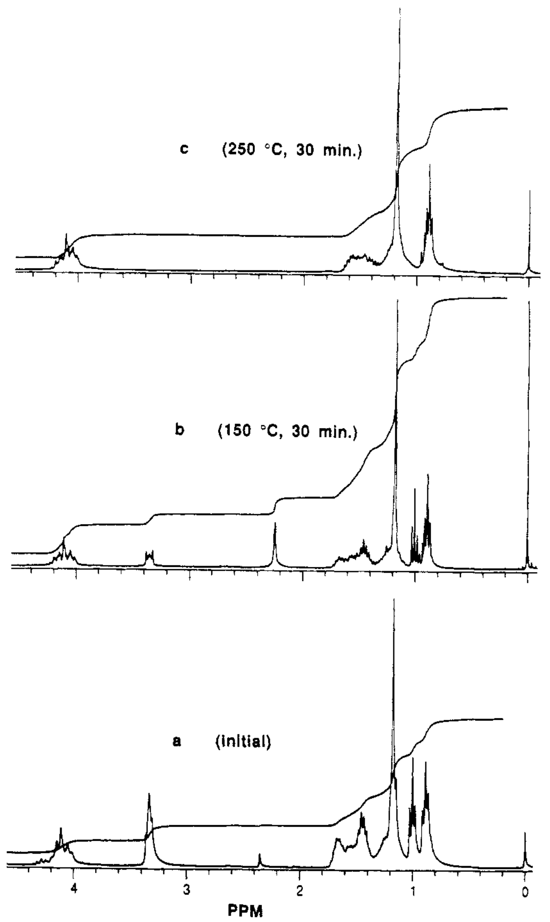


Figure 2. Proton NMRs of poly-MPPL-COO$^-$ $^+NBu_4$ tetramer showing thermal degradation of $^+NBu_4$. Spectra show (a) initial sample, (b) sample heated to 150 °C for 30 min, and (c) sample heated to 250 °C for 30 min.

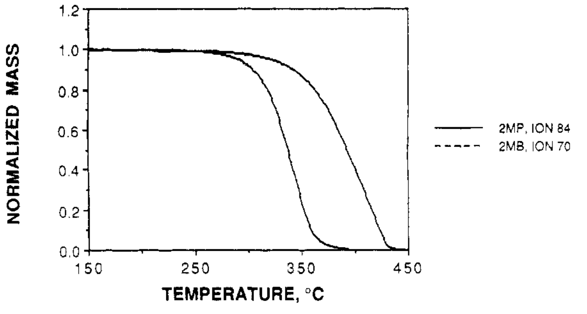


Figure 3. Comparison of TGAs of poly-MPPL-COOH and poly-MPPL-COOCs heated at 20 °C/min.

groups can be present at polymer degradation temperatures, which can further complicate the chemistry. These results combined with the observation that polymer degradation is counterion dependent (vide infra) emphasize the necessity of replacing the thermally unstable Bu_4N^+ cations with thermally stable cations.

The peak temperature for polymer degradation is dependent on the terminal carboxylate counterion. Table II lists the effect of carboxylate ion exchange on the polymer degradation temperature. Figure 3 compares a TGA from poly-MPPL-COOH and poly-MPPL-COOCs. The Bu_4P^+ carboxylate terminated polymer degrades 140 deg lower than the carboxylic acid terminated polymer. The reverse polymerization process, Scheme I, is dependent on the terminal carboxylate group acting as a nucleophile toward the next main-chain methylene to displace another carboxylate group. It is well-known that anion nucleophilicity is cation dependent.[16,17] For solvent-separated ion pairs (SSIP), anion nucleophilicity appears to increase as the cation is changed in the order $Li^+ > Na^+ > K^+ > Cs^+$. This trend is probably a reflection of the degree of ion pair dissociation. However, for contact ion pairs (CIP) the nucleophilicity order is reversed, i.e., $Cs^+ > K^+ > Na^+ > Li^+$. We would anticipate that the carboxylate groups would be ion paired in the low dielectric environment of the polymer melt. Apparently Bu_4P^+ creates a much more nucleophilic CIP than the alkali ions. The observed effect of the nucleophilicity of the terminal carboxylate group on degradation supports a reverse polymerization mechanism.

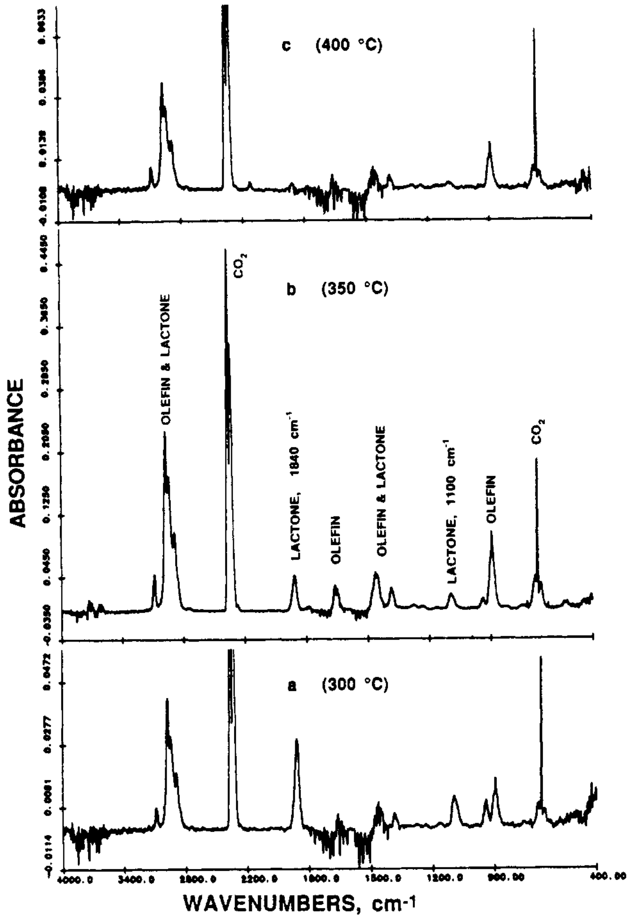


Figure 4. FTIR of evolved gases from poly-MPPL-COOCs (M_n = 117 000) at 300, 350, and 400 °C.

Lactone reformation during thermal degradation can be observed by TGA/FTIR. The lactone has a distinct IR-active carbonyl stretch at 1834 cm^{-1}. FTIR analysis of the evolved gases during degradation of poly-MPPL-COO$^-$ ^+Cs at 250 °C shows weak signals at 2900, 1834, 1100, and 960 cm^{-1} all due to the lactone. As the temperature is increased, the evolved gas increases but the amount of lactone relative to CO_2 decreases. Figure 4 shows a series of FTIR spectra of the evolved gas during degradation of poly-MPPL-COO$^-$ ^+Cs at 300, 350, and 400 °C. At 300 °C the major product is lactone but by 400 °C there is essentially no lactone observed. The reason for the disappearance of lactone is its inherent instability at the polymer degradation temperature, i.e., lactone is still a major product but it degrades very quickly to CO_2 and olefin. The thermal degradation of β-propiolactone is a first-order process with Arrhenius parameters of E_a = 191.4 kcal/mol and $A = 1.2 \times 10^{16}$ s^{-1}.[18] If we assume that alkylated lactones degrade at similar rates, we can estimate that the lactone will have lifetimes of 1000, 20, <1, and <0.1 s at 250, 300, 350, and 400 °C,

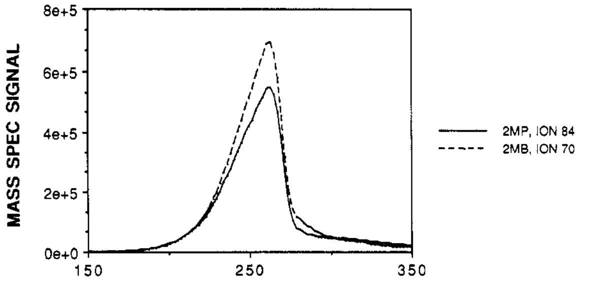


Figure 5. Appearance of 2-methylbutene and 2-methylpentene during the thermal degradation of randomly copolymerized poly-MPPL|MEPL-COO$^-$ $^+$PBu$_4$.

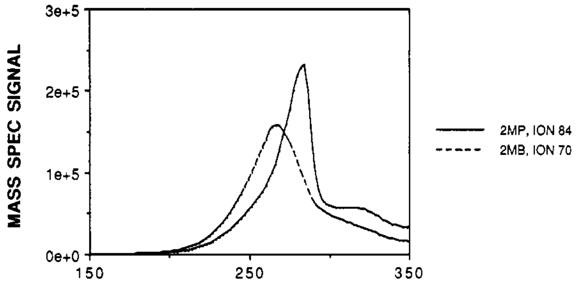


Figure 6. Appearance of 2-methylbutene and 2-methylpentene during the thermal degradation of block copolymerized poly-MPPL||MEPL-COO$^-$ $^+$PBu$_4$.

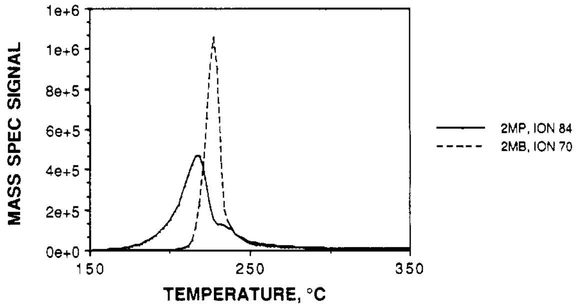


Figure 7. Appearance of 2-methylbutene and 2-methylpentene during the thermal degradation of block copolymerized poly-MEPL||MPPL-COO$^-$ $^+$PBu$_4$.

respectively.

Reverse polymerization requires that the carboxylate end of the polymer chain decomposes before the initiator end. It follows that during thermal degradation of block copolymers, products from the terminal block will appear before those from the initial block. With this expectation in mind we have studied the thermal degradation of random (B|A) and block (B||A) copolymers of 2-methyl-2-propyl-3-propiolactone with 2-methyl-2-ethyl-3-propiolactone (poly-MPPL|MEPL-COO$^-$ $^+$PBu$_4$, M_n = 97 600, M_w/M_n = 1.12; poly-MPPL||MEPL-COO$^-$ $^+$PBu$_4$, M_n = 68 400, M_w/M_n = 1.14; and poly-MEPL||MPPL-COO$^-$ $^+$PBu$_4$, M_n = 29 900, M_w/M_n = 1.12). Figures 5–7 show TGA/MS results from these three polymers. When the random copolymer is heated at 20 °C/min (Figure 5), 2-methylbutene (2-MB, formed by the thermal decomposition of 2-methyl-2-ethyl-3-propiolactone, m/e = 70) and 2-methylpentene (2-MP, formed by the thermal decomposition of 2-methyl-2-propylpropiolactone, m/e = 84) appear simultaneously along with CO$_2$, indicating no inherent preference for formation of either lactone. In contrast, when poly-MPPL||MEPL-COO$^-$ $^+$PBu$_4$ is heated at 20 °C/min (Figure 6), 2-MB appears prior to 2-MP, consistent with initial degradation of the carboxylate end. More polymer degrades above 300 °C than we expect under these conditions (suggesting that not all of the carboxylate end groups were ion exchanged), but the time lag between MPPL and MEPL is nonetheless considerable. The expected opposite result is obtained when poly-MEPL||MPPL-COO$^-$ $^+$PBu$_4$ is heated at 20 °C/min (Figure 7); i.e., 2-MP appears prior to 2-MB. Polymer with Bu$_4$P$^+$ counterion was used for this experiment to be certain thermal degradation occurred at a temperature where the random-scission mechanism does not contribute to degradation.[1] These data confirm that the carboxylate end of the polymer chain degrades significantly prior to the initiator end of the chain. It is likely that intermolecular transesterification will compete with intramolecular reverse polymerization. The intermolecular process will lead to loss of discrete A||B blocks and broadening of the MW distribution. Although we observe some broadening of the MW distribution in isothermal degradation experiments (vide infra), the above results indicate that the intermolecular process is a minor reaction when the sample is heated at 20 °C/min. We conclude that the degradation process is a "living depolymerization" with all chain ends active simultaneously.

At this point it is useful to develop a general kinetic model of "living depolymerization" for comparison to our observations. If $P_{(n,t)}$ denotes the number of molecules of DP = n in the system at time t, then eq 1 describes the time evolution of $P_{(n,t)}$:

$$dP_{(n,t)}/dt = k_r(P_{(n+1,t)} - P_{(n,t)}) + k_p(P_{(n-1,t)} - P_{(n,t)})[\text{monomer}] \quad (1)$$

where k_r is the rate of lactone formation (reverse polymerization) and k_p is the rate of polymerization. From eq 1 it can be shown that the polymer mass will follow eq 2 during degradation if all the monomer is removed from the system before it can repolymerize (i.e., [monomer] = 0).

$$dM/dt = -k_r\sum_n P_n = -k_r[\text{total no. of molecules}] \quad (2)$$

We estimate, on the basis of the rate of monomer production combined with the rate monomer reacts with the living chain end (k_{obs} = k_p[monomer][living ends]) and leaves the sample ($\tau \sim 0.1$ s), that less than 1% of monomer produced by reverse polymerization is reincorporated into the polymer under our experimental conditions. During the initial stages of degradation the total number of molecules is constant so that

$$d(M/M_0)/dt = -k_r/\text{DP}_0 \quad (3)$$

where DP$_0$ is the degree of polymerization at $t = 0$. For systems with initial narrow molecular weight distributions ($M_w/M_n \sim 1.1$), computer modeling indicates eq 3 will hold up to 40% degradation after which time some chains will have been completely depolymerized. During this period the process will appear to follow zero-order kinetics. Figure 8 compares the isothermal degradation (200 °C) of poly-MPPL-COO$^-$ $^+$PBu$_4$ with DP$_0$'s of 51, 206, and 610. As expected, lower MW polymer degrades faster than higher MW polymer and degradation is close to zero order. However, the degradation rate slightly increases as the reaction proceeds. This effect is especially noticeable with the lower MW polymer. One speculative explanation is based on the observed sensitivity of k_r to the nature of the counterion: as degradation occurs the number of ionic end groups is constant but their concentration increases as the volume of the sample decreases. It is possible that k_r slightly increases with the concen-

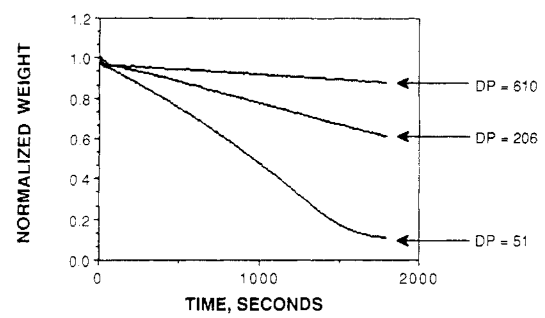


Figure 8. Isothermal degradation of poly-MPPL-COO$^-$ $^+PBu_4$ with DP of 51, 206, and 610 at 200 °C.

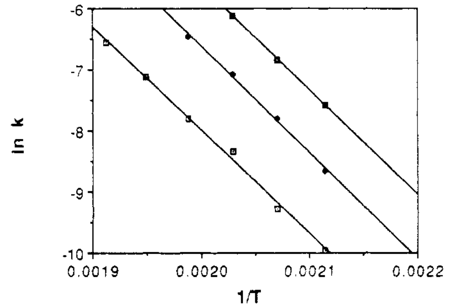


Figure 9. Arrhenius plots (ln (k_r) versus $1/T$) for the degradation of poly-MPPL-COO$^-$ $^+PBu_4$; DP_0 = 51; 206, and 610.

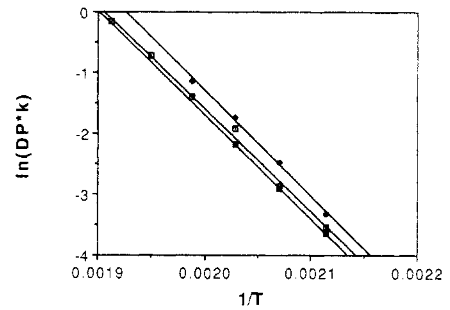


Figure 10. Arrhenius plots adjusted for the difference in DP_0 (ln (DP_0k_r) versus $1/T$) for the degradation of poly-MPPL-COO$^-$ $^+PBu_4$; DP_0 = 51, 206, and 610.

tration of ionic end groups.

Figure 9 shows Arrhenius plots (ln (k_r) versus $1/T$, assuming a zero-order process using data between 5 and 15% degradation) for the degradation of poly-MPPL-COO$^-$ $^+PBu_4$, DP_0 = 51, 206, and 610. Degradation has the same activation energy for all three molecular weights (143.2 ± 1 kJ/mol), but the Arrhenius preexponent increases as molecular weight decreases. In Figure 10 the data have been adjusted to take into account the difference in DP_0 (ln (DP_0k_r) versus $1/T$). Figure 10 indicates the degradation reaction has a constant frequency factor of $(2 \pm 1) \times 10^{14}$ s^{-1}. Similar experiments with poly-MPPL-COO$^-$ ^+Cs give an activation energy of 163 kJ/mol with a frequency factor of 3×10^{14} s^{-1}. The activation energy for degradation of poly-MPPL-COO$^-$ $^+PBu_4$ is about 38 kJ/mol above the minimum necessary to overcome ring strain during reformation of propiolactone. The frequency factor of 2×10^{14} s^{-1} is not out of the ordinary for unimolecular fission reactions but seems high for a process that must go through a four-membered ring transition state.[19] Comparison of poly-MPPL-COO$^-$ $^+PBu_4$ with poly-MPPl-COO$^-$ ^+Cs indicates the reverse polymerization rate difference for these two polymers is predominantly due to a 20 kJ/mol difference in the activation barrier.

Kinetic effects on molecular weight distributions from living polymerization are well understood. When k_p[monomer] $\gg k_r$ (i.e., polymerization is irreversible) a Poisson distribution results for the number fraction that broadens with the square root of the reaction time.[20] This produces a decrease in M_w/M_n as the reaction proceeds and leads to the narrow molecular weight distributions commonly associated with living polymerizations. In contrast, when k_p[monomer] $\sim k_r$ (the reaction is reversible) a most probable distribution is produced.[23-25] However, to our knowledge there has been no previous demonstration or discussion of the case where $k_r \gg k_p$[monomer], a condition that exists only if monomer is removed from the system faster than it repolymerizes. It is the case where $k_r \gg k_p$[monomer] that we will call living depolymerization. We do not expect the molecular weight distributions to deevolve along the same path that living polymerization takes. For example, it is certain that the number fraction distribution cannot decrease during degradation, which alone will cause an increase in M_w/M_n. Furthermore we anticipate that the number fraction distribution should continue to broaden with the square root of the reaction time, which will further increase M_w/M_n.

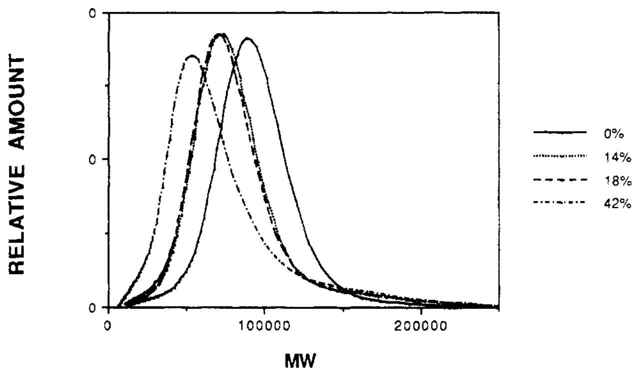


Figure 11. Weight-average distributions for MPPL-COO$^-$ $^+PBu_4$ after 0, 14, 18, and 42% degradation at 240 °C.

For the case where the reaction is proceeding in only one direction ($k_r \gg k_p$[monomer]), solutions to eq 1 have the property

$$P_{(n,t)} = P_{(n+k_rt,t=0)} \qquad (4)$$

so that the molecular weight of the polymer will systematically decrease during degradation and, if we know the form of the initial distribution, we can predict the form of the distribution at a later time, t. To model the system we assume that the initial distribution is described by the Schulz–Zimm distribution:[21,22]

$$P_{(n,t=0)} = cn^ze^{-n/y} \qquad (5)$$

where $M_w/M_n = z + 2/z + 1$, c is a normalization factor, and $DP_0 = y(z + 1)$. Thus if we wish to start with an initial $M_w/M_n = 1.1$ and $DP_0 = 50$ we can choose $z = 9$ and $y = 5$. Combination of eq 5 with eq 4 gives eq 6, which describes the distribution at time t.

$$P_{(n,t)} = c(n + k_rt)^ze^{-(n+k_rt)/y} \qquad (6)$$

Using eq 6, we can calculate M_w/M_n and DP as functions of polymer degradation.

Figure 11 shows weight-average distributions for MPPL-COO$^-$ $^+PBu_4$ after 0, 14, 18, and 42% degradation. It is immediately apparent that the overall shape of the distributions do not vary significantly and the peak shifts toward the origin as degradation proceeds. A plot of DP/DP_0 versus the fraction of polymer degraded (M/M_0), Figure 12, indicates that DP systematically decreases. As DP decreases we observe a simultaneous increase in

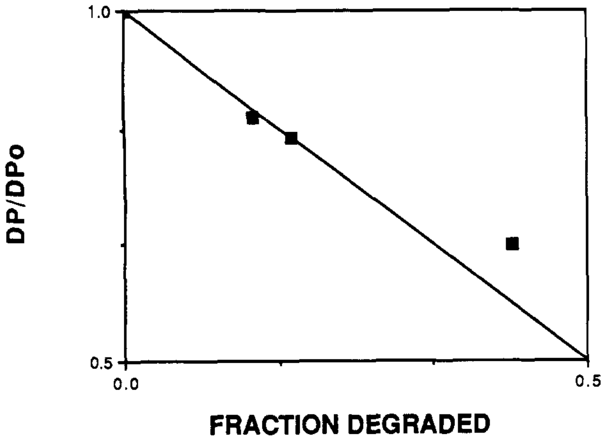


Figure 12. Plot of DP/DP_0 versus the fraction of $MPPL\text{-}COO^{-}\,{}^{+}PBu_4$ degraded.

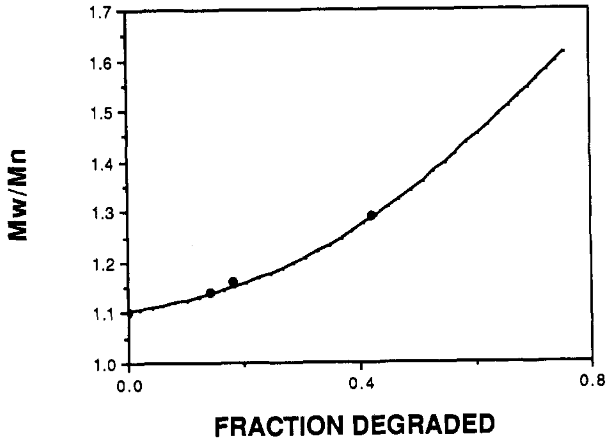


Figure 13. Calculated and observed values of M_w/M_n versus fraction of sample degraded.

M_w/M_n from 1.10 at 0% degradation to 1.14, 1.16, and 1.30 at 14, 18, and 42% degradation, respectively. Figure 13 plots M_w/M_n versus percent degradation calculated from eq 6 along with the experimentally observed values. The excellent agreement further supports the proposal that this is a living depolymerization.

It is necessary to address the formation of larger cyclic oligomers observed by direct pyrolysis–mass spectrometry (DP–MS) of poly(2,2-dimethyl-3-hydroxypropionic acid) (polypivalolactone).[11-13] Larger cyclic oligomers appear to account for less than 1% (on the basis of ion intensities in reported MS data) of the overall degradation products of polypivalolactone. Our experimental setup will not detect larger cyclic oligomers. However, on the basis of the mechanism proposed in Scheme I, we anticipate that both transesterification and formation of larger cyclic oligomers must compete with reverse polymerization. Kinetic parameters for these two competing reactions cannot be determined from our data but it is certain they will have different activation energies and frequency factors than the reverse polymerization process. We believe that under most conditions reverse polymerization will dominate transesterification or cyclic oligomer formation.

Conclusions

We have demonstrated that the thermal degradation of poly(2,2-dialkyl-3-hydroxypropionic acid)s with anionic carboxylate end groups proceeds by reverse polymerization with reformation of propiolactone monomer. Degradation of block copolymers has demonstrated that the polymer degrades from the carboxylate terminus toward the initiator end of the chain. Under some conditions, the process is a "living depolymerization" with all chains degrading simultaneously. We believe the results observed for 2,2-dialkyl-3-propiolactones will be general for polymerizations that are permanently living.

The next paper in this series will describe a random-scission-initiated degradation process for poly(2,2-dialkyl-3-hydroxypropionic acid)s that occurs at higher temperatures when the terminal carboxylate group is protonated or esterified.

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Registry No. MPPL (homopolymer), 25188-77-6; MPPL (SRU), 25265-42-3; (MPPL)(MEPL) (block copolymer), 125518-34-5; (MPPL)(MEPL) (copolymer), 125495-97-8; MMPL (homopolymer), 24969-13-9; MMPL (SRU), 24937-51-7; (MPPL)·Li (homopolymer), 125495-93-4; (MPPL)·Li (SRU), 125495-98-9; (MPPL)·Na (homopolymer), 125495-94-5; (MPPL)·Na (SRU), 125495-99-0; (MPPL)·K (homopolymer), 125495-95-6; (MPPL)·K (SRU), 125496-00-6; (MPPL)·Cs (homopolymer), 125495-96-7; (MPPL)·Cs (SRU), 125496-01-7.